Highly Selective Allylation of Alkyl Methyl Ketones in the Presence of Chiral 2-Amino Alcohol Derivatives

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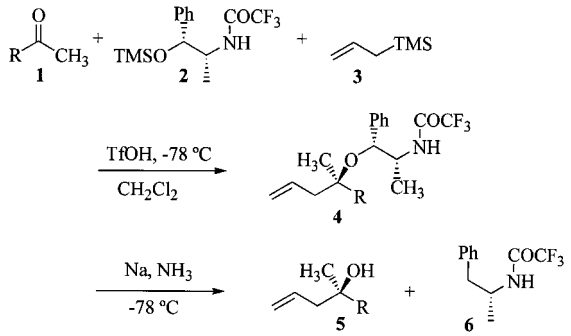
The facial selective allylation of alkyl methyl ketones **1a–f** in the presence of chiral 2-amino alcohol derivatives **2a–p** by reaction with allylsilane **3** and a catalytic amount of TfOH to give the tertiary homoallylic ethers **8a–o** and **9a–e** is described. The best results were obtained with the 2-amino alcohol derivative **2p** which affords a stereoselectivity of 18:1 even for the allylation of ethyl methyl ketone. The ethers **8** and **9**, which contain a phenyl group at C-1 of the amino alcohol moiety, can be cleaved to give the corresponding homoallylic alcohols **5** by reduction with sodium or lithium in liquid ammonia.

Introduction

One of the most difficult problems in asymmetric synthesis is facial-selective addition to aliphatic ketones. Thus, many reagents which give excellent asymmetric induction with aldehydes[1][2][3][4][5] fail in the case of ketones. However, recently we have shown that aliphatic ketones **1** can easily be allylated to give tertiary homoallylic alcohols **5** with an enantiomeric excess *ee* > 92%.[6]

Scheme 1. Allylation of alkyl methyl ketones **1**



The reaction proceeds in a domino-type fashion[7] by mixing the ketone **1** and the trimethylsilyl ether of *N*-(trifluoroacetyl)norpseudoephedrine (**2**) and allylsilane **3** in the presence of a catalytic amount of trifluoromethanesulfonic acid (TfOH) at −78°C for 1−3 h. The corresponding homoallylic ethers **4** are obtained in a very clean transformation, usually in excellent yield and with high diastereoselectivity of up to >96:4 means that the best selectivities are >96:4; >96:4 means that we did not see the other diasteromer. The chiral auxiliary in **4** can easily be removed by reductive cleavage using lithium or sodium in liquid ammonia to give the desired chiral nonracemic homoallylic alcohols **5** and the amphetamine derivative **6**.

In a similar way, aliphatic aldehydes can also be allylated using **2** and allylsilane **3** in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) to give the corresponding secondary homoallylic ethers with a diastereoselectivity of > 99:1;[8] for this reaction the oxazolidinium ion **7a** was demonstrated to be an intermediate by on-line NMR spectroscopy.[9] It was also shown that the obtained diastereoselectivity decreases dramatically using the corresponding ephedrine derivative instead of **2a**. Thus, the highly stereoselective formation of **7a** must be controlled by both stereogenic centres C-1 and C-2. In addition, it was found that the configurations of the newly formed stereogenic centres in the homoallylic ethers are opposite depending on whether aldehydes or ketones are used. This clearly implies that the mechanism of the two transformations must be different. Whereas the mechanism of the allylation of aldehydes using the described procedure could be clarified, an explanation for the obtained excellent selectivity in the allylation of ketones cannot so far be given; however, an oxazolidinium ion **7b**, as proposed for the reaction of aldehydes, can be excluded as a possible intermediate.

Here we describe our efforts in the design of new chiral reagents for the allylation of ketones. The following questions have been addressed: (1) Is it necessary to use chiral 2-amino alcohols with two stereogenic centres or can one centre be omitted? (2) Is the amino moiety an essential part of the auxiliary? (3) Which protecting group at the nitrogen atom is most suitable? (4) Can the diastereoselectivity be improved by employing new auxiliaries? For these investi-

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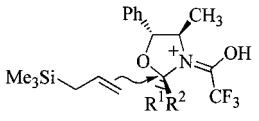
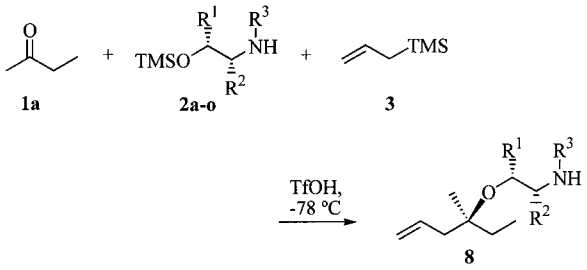
gations we used the allylation of ethyl methyl ketone (**1a**), being the most difficult substrate, as the standard.

Figure 1. Oxazolidinium ion **7a** as intermediate in the allylation of aldehydes



3 **7a:** R^1 = alkyl, R^2 = H
7b: R^1 = alkyl, R^2 = CH

Scheme 2. Allylation of **1a** in the presence of the 2-amino alcohol derivatives **2a−p**



Results and Discussion

All new chiral reagents were examined under the following standard conditions: One equivalent of the reagent, two equivalents of ethyl methyl ketone (**1a**) and two equivalents of allylsilane **3** were dissolved in dichloromethane and cooled to −78°C. Then, 0.2 equivalents of a 1:1 mixture of trimethylsilyl triflate and triflic acid were added to start the reaction. After 24 hours, the reaction was quenched by addition of triethylamine and the ratio of the formed diastereomeric homoallylic alcohols **8a−p** determined by ^{13}C-NMR spectroscopy of the crude mixture; the reaction was usually already complete after 2−3 hours, but longer reaction times do not influence the yield und the selectivity of the allylation. With the norpseudoephedrine derivative **2a** containing an *N*-trifluoroacetyl group, a diastereoselectivity of 9:1 was found at −78°C and of 24:1 at −109°C using a 1:1 mixture of dichloromethane and freon as a solvent. In order to optimize the structure of the reagent **2,** first the protecting group at the nitrogen atom was varied. The protecting group was chosen with attention to any steric or electronic effects. Using the trichloroacetyl moiety as in **2b** the yield was decreased (71%) and the selectivity slightly increased (9.5:1). The strong electron-withdrawing group trifluoromethanesulfonyl, as in **2c**, was not sufficiently stable and the yields and the diastereoselectivity were decreased (30%, 6.5:1). On the other hand, acyl groups with a low electron-withdrawing effect such as acetyl as in **2d** could not be used since such compounds do not react. This is in accordance with the proposed mechanism, in which at first a proton attacks the carbonyl group of the ketone. If the basicity of the carbonyl group of the amide moiety is too high, the reaction cannot proceed. If one omits the *N*-acylamino group completely, as in **2e**, the reaction still proceeds, although the diastereoselectivity drops to 1.8:1. This clearly shows that the *N*-acyl group is an important part of the auxiliary, although we do not, as yet, know its exact function.

On the basis that the trifluoroacetyl group seemed to be the best protecting group at the nitrogen atom we prepared the different 2-amino alcohol derivatives **2f−p** and proved their usefulness in the allylation of ethyl methyl ketone (**1a**, Table 1). It was found that the stereogenic centre C-2 in **2a** seems to have only a small effect on the diastereoselectivity, since **2f** gave the same result as found with **2a**. As expected the use of **2g**, which only has a stereogenic centre in C-2, gave a poor selectivity (1.5:1). With increasing bulkiness of the phenyl substituent in **2f**, as in **2h−2j**, a small increase in selectivity from 9:1 to 13:1 was observed. In contrast, using the derivatives **2k** and **2l** the desired products could not be obtained, probably due to an electronic phenomenon. In both cases, an allylation of the chiral reagent with a loss of the stereochemical information had occurred. We propose the intermediate formation of a stabilized benzylic cation which reacts with allylsilane **3**.

Table 1. Allylation of ketone **1a** in the presence of **2a−p**

2	R^1	R^2	R^3	**8**: yield [%]	d.r.[a]
a[b]	Ph	Me	$COCF_3$	80	9.0:1
b[b]	Ph	Me	$COCCl_3$	71	9.5:1
c[b]	Ph	Me	SO_2CF_3	30	6.5:1
d[b]	Ph	Me	$COCH_3$	< 1	–
e	[c]	[c]	[c]	81	1.8:1
f	Ph	H	$COCF_3$	90	9.0:1
g	H	Ph	$COCF_3$	99	1.5:1
h	2-MeC_6H_4	H	$COCF_3$	60	10:1
i	2,6-$Cl_2C_6H_3$	H	$COCF_3$	57	11:1
j	1-Naph	H	$COCF_3$	92	13:1
k	2,4,6-$Me_3C_6H_2$	H	$COCF_3$	< 1	–
l	4-$MeOC_6H_4$	H	$COCF_3$	< 1	–
m[b]	Me	H	$COCF_3$	79	6.1:1
n[b]	*i*Pr	H	$COCF_3$	74	7.5:1
o	*t*Bu	H	$COCF_3$	30	2.0:1
p[d]	Ph	Ph	$COCF_3$	**9a**: 95	18:1

[a] Determined by ^{13}C-NMR spectroscopy. – [b] The reaction was performed with *ent*-**2** to give *ent*-**8**. – [c] Racemic *O*-trimethylsilyl-1-phenylethanol was used. – [d] The reaction was performed with *(1S,2R)*-**2p**.

Exchanging the phenyl group in **2f** by a methyl group, as in **2m**, led to a decrease in selectivity in the allylation; a slightly better result was obtained with **2n.** Surprisingly, **2o** with a *tert*-butyl group at C-1 gave an astoundingly low selectivity (2:1). Thus, the *tert*-butyl group might be too bulky to allow the formation of a pocket in the transition structure into which the methyl group of the ketone **1a** could fit. However, one should keep in mind that reagents **2** with an alkyl group at C-1 are anyway not very suitable, since they cannot easily be removed after the allylation.

By far the best diastereoselectivity was found in the reaction using the 1,2-diphenylamino alcohol derivative **2p** to give the corresponding homoallylic ether **9a** in a ratio of 18:1 with 60% yield after 24 h. The yield could be improved by prolonging the reaction time; thus, after four days **9a** was obtained in 95% yield (Table 2). To show the usefulness of **2p**, the facial selective allylation of the ketones **1b−f** to

give **9a−f** was investigated (Table 2). In all cases, except for **1c**, a selectivity of 18:1 or even higher was found; thus, methyl cyclohexyl ketone (**1e**) gave a diastereoselectivity of 38:1, but for the sterically hindered ketones the conversion was rather slow; *tert*-butyl methyl ketone did not react at all under these conditions. Therefore it is advisable to use **2a** or **2f** instead of **2p** as a reagent for the allylation of bulky ketones. A strange result was found for the allylation of methyl pentyl ketone (**1c**) in the presence of **2p** for which only a 9:1 ratio was obtained. The assignment of the configuration of the products was performed in analogy to **4** with R = $(CH_2)_2C_6H_5$ and R = $CH(CH_3)_2$ for which X-ray structure determinations exist.[6]

The auxiliary in **9** can be removed as easily, as found for the norpseudoephedrine moiety in **4.** Using excessive sodium in liquid ammonia at −78°C the homoallylic ether **9b** was transformed into the corresponding homoallylic alcohol **5** (R = *n*-pentyl) in 88% yield.

Scheme 3. Allylation of ketones **1a−e** in the presence of the chiral 2-amino alcohol derivative **2p**

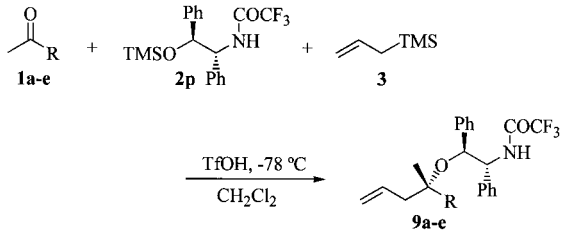


Table 2. Allylation of ketones **1a−f** in the presence of **2p**

1	R	reaction time	**9**: yield [%]	d.r.[a]
a	ethyl	24 h/4 d	60/95	18:1
b	propyl	6 h	57	18:1
c	pentyl	4 d	53	9:1
d	isopropyl	3 d	20	35:1
e	cyclohexyl	3 d	14	38:1
f	*tert*-butyl	4 d	< 1	−

[a]Determined by ^{13}C-NMR spectroscopy of the crude product mixture.

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Experimental Section

General: All reactions were performed in oven-dried glassware under nitrogen unless otherwise noted. Melting points were determined with a Mettler FP61 and are uncorrected. Optical rotations were measured with a Perkin−Elmer 241 digital polarimeter in a 1-dm cell. IR spectra were recorded with a Bruker IFS 25 FT-IR instrument, and ^{1}H-NMR and ^{13}C-NMR spectra with a Bruker AM-300 and a Varian VXR-200. Chemical shifts were reported on the δ scale relative to $CDCl_3$ as an internal standard. Mass spectra were measured at 70 eV with a Varian MAT 311A. GC analysis was carried out with hydrogen as the carrier gas using a DB 1701 column (J and W Scientific, 0.25 mm × 50 m). HPLC analysis was carried out using Nucleosil 5C18 (250 mm, 5 μm). TLC chromatography was performed using precoated silica gel SIL G/UV_{254} plates (Macherey, Nagel and Co.), and silica gel 32−63 (0.032−0.064 mm, Macherey, Nagel and Co.) was used for column chromatography. Microanalyses were carried out by the Mikroanalytisches Labor des Instituts für Organische Chemie der Universität Göttingen.

General Procedure 1: Reaction of Ethyl Methyl Ketone (**1a**)*, Allylsilane* **3** *and the Chiral Reagents* **2**: To a solution of ethyl methyl ketone (**1a**, 2.00 mmol), the chiral reagents **2a−p** (1.00 mmol) and allyltrimethylsilane (**3**, 228 mg, 2.00 mmol) in CH_2Cl_2 (4 ml) was added with stirring at −78°C a 1:1 mixture of TfOH (0.10 mmol) and TMSOTf (0.10 mmol) or pure TfOH (0.20 mmol). The stirring was continued at −78°C. The reaction was quenched by addition of triethylamine (160 μl), the mixture was poured into water (10 ml), the organic phase separated and the aqueous phase extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel gave the corresponding homoallylic ethers **8a−o** and **9a.**

(4S,1′R,2′R)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenylpropoxy)-hex-1-ene (**8a**): According to the general procedure 1, reaction of **2a** (319 mg, 1.00 mmol) for 1 h have the homoallylic ether **8a** (282 mg, 0.80 mmol, 80%) as colourless needles; 32 mg of **2a** were recovered (0.10 mmol, 10%). M.p. 67°C, $[\alpha]_D^{20}$ = +11.0 (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 3 H), 1.00 (s, 3 H), 1.21 (d, *J* = 7.0, 3 H), 1.41 (q, *J* = 7.0 Hz, 2 H), 2.27−2.38 (m, 2 H), 4.07 (m, 1 H), 4.57 (d, *J*= 4.0 Hz, 1 H), 5.04−5.17 (m, 2 H), 5.73−5.95 (m, 1 H), 6.48 [d (b), *J* = 7.5 Hz, 1 H], 7.20−7.37 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.47, 17.15, 23.09, 32.23, 43.25, 52.12, 74.37, 79.32, 116.02 (q, $^1J_{CF}$ = 285 Hz), 117.91, 126.73, 127.§1, 128.32, 134.44, 141.82, 156.51 (q, $^1J_{CF}$ = 35 Hz). − IR (KBr): ν = 3308 cm^{-1}, 3110, 3088, 3032, 2938, 2884, 1726, 1704, 1566, 1208, 1186, 1164, 1082, 912, 762, 726, 702. − MS (70 eV, EI): *m/z* (%) 302 (1), 230 (100), 107 (35), 97 (16), 69 (3). − $C_{18}H_{24}F_3NO_2$ (343.4): calcd. C 62.96, H 7.04; found C 63.10, H 7.08.

(4R,1′S,2′S)-4-Methyl-4-(1′-phenyl-2′-trichloroacetamido-1′-propoxy)-1-hexene (**8b**): According to the general procedure 1, reaction of **2b** (369 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8b** (282 mg, 0.71 mmol, 71%) as a colorless oil. $[\alpha]_D^{20}$ = +15.0 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 8.0 Hz, 3 H), 1.01 (s, 3 H), 1.23 (d, *J* = 6.5 Hz, 3 H), 1.42 (q, *J* = 8.0 Hz, 2 H), 2.33 (d, *J* = 8.0 Hz, 2 H), 3.93−4.12 (m, 1 H), 4.63 (d, *J* = 3.0 Hz, 1 H), 5.09 (d, *J* = 12 Hz, 1 H), 5.11 (d, *J* = 16 Hz, 1 H), 5.83 (ddd, *J* = 16, 12, 8.0 Hz, 1 H), 6.91 [d(b), *J* = 8.0 Hz, 1 H], 7.19−7.39 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.42, 16.98, 22.98, 32.08, 43.22, 53.29, 74.04, 79.19, 117.75, 126.68, 127.59, 128.10, 134.26, 141.65, 160.94. − IR (film): ν = 3334 cm^{-1}, 3030, 2974, 2936, 1690, 1642, 1530, 1142, 766, 700. − MS (70 eV, FD): *m/z* (%) = 278 (57), 203 (23), 117 (35), 97 (100).

(4R,1′S,2′S)-4-Methyl-4-(1′-phenyl-2′-trifluoromethanesulfonyl-1′-propoxy)-1-hexene (**8c**): According to the general procedure 1, reaction of **2c** (358 mg, 1.00 mmol) for 2 d gave the homoallylic ether **8c** (115 mg, 0.30 mmol, 30%) as a yellowish oil. $[\alpha]_D^{20}$ = +45.3 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3 H), 0.99 (s, 3 H), 1.21 (q, *J* = 7.5 Hz, 2 H), 1.35 (d, *J* = 6.0 Hz, 3 H), 2.30 (d, *J* = 7.5 Hz, 2 H), 3.60−3.82 (m, 1 H), 4.51 (d, *J* = 3.5 Hz, 1 H), 4.99−5.19 (m, 3 H), 5.68−5.96 (m, 1 H), 7.19−7.43 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.44, 18.50, 23.16, 32.20, 43.19, 57.30, 75.59, 79.58, 118.08, 119.50 (q, $^1J_{CF}$ = 320 Hz), 126.33, 127.37, 128.39, 134.46, 140.66. − IR (film): ν = 3304 cm^{-1}, 3032, 2968, 1494, 1452, 1416, 1230, 1156, 1148, 752, 702.

(±)-4-Methyl-4-(1′-phenyl-1′-ethoxy)-1-hexene (**8e**): According to the general procedure 1, reaction of **2e** (194 mg, 1.00 mmol) for

16 h gave the homoallylic ether **8e** (176 mg, 0.81 mmol, 81%) as a colorless oil. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 8.0 Hz, 3 H), 1.01 (s, 3 H), 1.39 (d, *J* = 6.5 Hz, 3 H), 2.12–2.42 (m, 2 H), 4.67 (q, *J* = 8.0 Hz, 1 H), 5.01 (d, *J* = 16 Hz, 1 H), 5.04 (d, *J* = 10 Hz, 1 H), 5.70–5.97 (m, 1 H), 7.17–7.41 (m, 5 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 9.49, 24.51, 28.02, 32.91, 44.64, 70.77, 79.45, 118.21, 126.89, 127.76, 129.34, 136.24, 148.86; IR (film): ν = 3074 cm^{-1}, 3026, 2974, 1492, 1374, 1146, 1084, 760, 700. – MS (70 eV, FD): *m/z* (%) = 177 (22), 105 (100), 77 (25).

(4S,1′R)-4-Methyl-4-(1′-phenyl-2′-trifluoroacetamido-1′-ethoxy)-1-hexene (**8f**): According to the general procedure 1, reaction of **2f** (305 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8f** (297 mg, 0.90 mmol, 90%) as a colorless oil. $[\alpha]_D^{20}$ = −64.5 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 7.5 Hz, 3 H), 1.00 (s, 3 H), 1.41 (q, *J* = 7.5 Hz, 2 H), 2.27 (d, *J* = 7.5 Hz, 2 H), 3.25 (ddd, *J* = 13, 8.5, 4.5 Hz, 1 H), 3.64 (ddd, *J* = 13, 7.0, 4.5 Hz, 1 H), 4.67 (dd, *J* = 8.5, 4.5 Hz, 1 H), 5.08 (d, *J* = 16 Hz, 1 H), 5.10 (d, *J* = 12 Hz, 1 H), 5.83 (ddd, *J* = 16, 12, 7.5 Hz, 1 H), 6.62–6.85 (m, 1 H), 7.23–7.39 (m, 5 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.37, 23.22, 32.28, 43.31, 46.99, 71.85, 79.38, 116.02 (q, $^1J_{CF}$ = 288 Hz), 118.14, 126.38, 128.04, 128.63, 134.20, 142.06, 157.10 (q, $^2J_{CF}$ = 37 Hz). – IR (KBr): ν = 3322 cm^{-1}, 3078, 2976, 2940, 1712, 1554, 1454, 1210, 1178, 702. – MS (70 eV, FD): *m/z* (%) = 288 (20), 216 (100), 97 (43), 55 (27), 41 (6). – $C_{17}H_{22}F_3NO_2$ (329.4): calcd. C 61.99, H 6.73; found C 61.87, H 6.87.

(4S,1′R)-4-Methyl-4-(1′-phenyl-1′-trifluoroacetamido-2′-ethoxy)-1-hexene (**8g**): According to the general procedure 1, reaction of **2g** (305 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8g** (325 mg, 0.99 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = −61.3 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 7.5 Hz, 3 H), 1.09 (s, 3 H), 1.39–1.56 (m, 2 H), 2.22 (d, *J* = 7.0 Hz, 2 H), 3.57 (dd, *J* = 10, 5.0 Hz, 1 H), 3.69 (dd, *J* = 10, 4.0 Hz, 1 H), 4.00–5.14 (m, 3 H), 5.62–5.86 (m, 1 H), 7.14–7.38 (m, 6 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.63, 22.32, 30.46, 42.20, 53.84, 63.11, 77.18, 115.78 (q, $^1J_{CF}$ = 288 Hz), 117.76, 126.78, 127.88, 128.52, 133.91, 138.46, 156.47 (q, $^2J_{CF}$ = 37 Hz). – IR (film): ν = 3316 cm^{-1}, 3034, 2974, 1708, 1640, 1458, 1208, 1170, 758, 700. – MS (70 eV, EI): *m/z* (%) = 288 (6), 216 (100). – $C_{17}H_{22}F_3NO_2$ (329.4): calcd. C 61.99, H 6.73; found C 62.10, H 6.62.

(4S,1′R)-4-Methyl-4-[1′-(2″-methylphenyl)-2′-trifluoroacetamido-1′-ethoxy]-1-hexene (**8h**): According to the general procedure 1, reaction of **2h** (319 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8h** (205 mg, 0.60 mmol, 60%) as colorless needles. M.p. 81°C; $[\alpha]_D^{20}$ = −43.3 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.75 (t, *J* = 7.5 Hz, 3 H), 0.93 (s, 3 H), 1.36 (q, *J* = 7.5 Hz, 2 H), 2.22 (d, *J* = 7.5 Hz, 2 H), 2.35 (s, 3 H), 3.08 (ddd, *J* = 14, 9.0, 4.5 Hz, 1 H), 3.65 (ddd, *J* = 14, 8.0, 3.5 Hz, 1 H), 4.84 (dd, *J* = 9.0, 3.5 Hz, 1 H), 5.05 (d, *J* = 17 Hz, 1 H), 5.07 (d, *J* = 13 Hz, 1 H), 5.80 (ddd, *J* = 17, 13, 7.5 Hz, 1 H), 6.66–6.89 (m, 1 H), 7.03–7.26 (m, 3 H), 7.34–7.50 (m, 1 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 9.53, 19.15, 23.11, 32.34, 43.39, 45.95, 68.47, 79.17, 116.30 (q, $^1J_{CF}$ = 288 Hz), 118.14, 126.30, 126.79, 127.71, 130.65, 133.82, 134.26, 140.16, 157.28 (q, $^2J_{CF}$ = 37 Hz). – IR (KBr): ν = 3398 cm^{-1}, 3102, 2974, 2944, 1704, 1560, 1462, 1210, 1180, 758. – MS (70 eV, FD): *m/z* (%) = 302 (1), 230 (100), 121 (62). – $C_{18}H_{24}F_3NO_2$ (343.4): calcd. C 62.96, H 7.04; found C 63.05, H 7.17.

(4S,1′R)-4-[1′-(2″,6″-Dichlorophenyl)-2′-trifluoroacetamido-1′-ethoxy]-4-methyl-1-hexene (**8i**): According to the general procedure 1, reaction of **2i** (374 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8i** (225 mg, 0.57 mmol, 57%) as a colorless oil. $[\alpha]_D^{20}$ = −48.0 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.67 (t, *J* = 7.0 Hz, 3 H), 0.94 (s, 3 H), 1.24–1.52 (m, 2 H), 2.20 (d, *J* = 6.5 Hz, 2 H), 3.67 (d, *J* = 7.0 Hz, 1 H), 3.71 (d, *J* = 7.0 Hz, 1 H), 5.00 (d, *J* = 12 Hz, 1 H), 5.02 (d, *J* = 16 Hz, 1 H), 5.37 (dd, *J* = 7.0, 7.0 Hz, 1 H), 5.76 (ddd, *J* = 16, 12, 6.5 Hz, 1 H), 6.80 [s(b), 1 H], 7.07 (t, *J* = 8.0 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.01, 22.65, 31.58, 42.05, 42.56, 68.67, 79.74, 115.79 (q, $^1J_{CF}$ = 288 Hz), 117.90, 128.38, 129.44, 130.63, 134.59, 135.41, 135.57, 157.06 (q, $^2J_{CF}$ = 37 Hz). – IR (film): ν = 3300 cm^{-1}, 3102, 2964, 1710, 1564, 1438, 1204, 1186, 778. – MS [70 eV, CI (NH_3)]: *m/z* (%) = 417 (63), 415 (100). – $C_{17}H_{20}Cl_2F_3NO_2$ (398.3): calcd. C 51.27, H 5.06; found C 51.45, H 5.10.

(4S,1′R)-4-Methyl-4-(1′-naphthyl-2′-trifluoroacetamido-1′-ethoxy)-1-hexene (**8j**): According to the general procedure 1, reaction of **2j** (355 mg, 1.00 mmol) for 3 d gave the homoallylic ether **8j** (350 mg, 0.92 mmol, 92%) as a colorless oil. $[\alpha]_D^{20}$ = −81.0 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 7.0 Hz, 3 H), 1.00 (s, 3 H), 1.43 (q, *J* = 7.0 Hz, 2 H), 2.33 (d, *J* = 7.0 Hz, 2 H), 3.32 (ddd, *J* = 12, 8.5, 4.0 Hz, 1 H), 3.86 (ddd, *J* = 12, 7.5, 3.5 Hz, 1 H), 5.10 (d, *J* = 11 Hz, 1 H), 5.12 (d, *J* = 17 Hz, 1 H), 5.48 (dd, *J* = 8.5, 3.5 Hz, 1 H), 5.87 (ddd, *J* = 17, 11, 7.0 Hz, 1 H), 6.72–6.94 (m, 1 H), 7.40–7.62 (m, 3 H), 7.64–7.93 (m, 3 H), 8.24 (d, *J* = 8.5 Hz, 1 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.41, 22.70, 32.03, 43.13, 46.35, 70.15, 79.43, 115.85 (q, $^1J_{CF}$ = 288 Hz), 117.96, 122.62, 124.65, 125.20, 125.70, 126.51, 128.28, 128.98, 133.73, 134.05, 137.48, 157.24 (q, $^2J_{CF}$ = 37 Hz). – IR (film): ν = 3318 cm^{-1}, 3068, 2968, 1708, 1550, 1210, 1172, 844, 802, 778. – MS (70 eV, FD): *m/z* (%) = 379 (5), 266 (100), 253 (65), 157 (17). – $C_{21}H_{24}F_3NO_2$ (379.4): HRMS (M^+): calcd. 379.1759; found 379.1759.

(4R,2′S)-4-Methyl-4-(1′-trifluoroacetamido-2′-propoxy)-1-hexene (**8m**): According to the general procedure 1, reaction of **2m** (243 mg, 1.00 mmol) for 2 d gave the homoallylic ether **8m** (210 mg, 0.79 mmol, 79%) as a colorless oil. $[\alpha]_D^{20}$ = +30.3 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 8.0 Hz, 3 H), 1.13 (s, 3 H), 1.16 (d, *J* = 7.0 Hz, 3 H), 1.43–1.59 (m, 2 H), 2.19 (d, *J* = 7.0 Hz, 1 H), 2.23 (d, *J* = 7.0 Hz, 1 H), 3.10–3.26 (m, 1 H), 3.36–3.52 (m, 1 H), 3.80–3.97 (m, 1 H), 5.07 (d, *J* = 16 Hz, 1 H), 5.08 (d, *J* = 12 Hz, 1 H), 5.80 (ddd, *J* = 16, 12, 7.0 Hz, 1 H), 6.58–6.87 (m, 1 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.12, 20.68, 22.94, 32.06, 43.37, 46.03, 64.77, 78.12, 115.99 (q, $^1J_{CF}$ = 289 Hz), 117.92, 134.23, 157.22 (q, $^2J_{CF}$ = 37 Hz,). – IR (film): ν = 3312 cm^{-1}, 3076, 2976, 2932, 1706, 1562, 1212, 1186. – MS (70 eV, FD): *m/z* (%) = 252 (1), 226 (4), 154 (100), 97 (24), 55 (26), 41 (23). – $C_{12}H_{20}F_3NO_2$ (267.3): calcd. C 53.92, H 7.54; found C 53.91, H 7.52.

(4R,2′S)-4-Methyl-4-(3′-methyl-1′-trifluoroacetamido-2′-butoxy)-1-hexene (**8n**): According to the general procedure 1, reaction of **2n** (271 mg, 1.00 mmol) for 2 d gave the homoallylic ether **8n** (219 mg, 0.74 mmol, 74%) as a colorless oil. $[\alpha]_D^{20}$ = +23.8 (*c* = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83–1.00 (m, 9 H), 1.14 (s, 3 H), 1.43–1.63 (m, 2 H), 1.66–1.92 (m, 1 H), 2.13–2.34 (m, 2 H), 3.39 (dd, *J* = 5.0, 5.0 Hz, 2 H), 3.44–3.62 (m, 1 H), 5.08 (d, *J* = 16 Hz, 1 H), 5.10 (d, *J* = 12 Hz, 1 H), 5.81 (ddd, *J* = 16, 12, 7.5 Hz, 1 H), 6.65–6.86 (m, 1 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.14, 16.62, 18.80, 22.41, 31.66, 32.07, 40.05, 43.53, 72.31, 78.05, 115.73 (q, $^1J_{CF}$ = 289 Hz), 117.82, 133.96, 156.76 (q, $^2J_{CF}$ = 37 Hz). – MS [70 eV, CI (NH_3)]: *m/z* (%) = 313 (100).

(4S,2′R)-4-(3′,3′-Dimethyl-1′-trifluoroacetamido-2′-butoxy)-4-methyl-1-hexene (**8o**): According to the general procedure 1, reac-

tion of **2o** (285 mg, 1.00 mmol) for 5 d gave the homoallylic ether **8o** (93 mg, 0.30 mmol, 30%) as a colorless oil. $[\alpha]_D^{20}$ = +23.8° (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.72 (s, 9 H), 0.73 (t, *J* = 7.5 Hz, 3 H), 1.01 (s, 3 H), 1.31−1.54 (m, 2 H), 2.11 (d, *J* = 6.5 Hz, 2 H), 2.92−3.12 (m, 1 H), 3.25−3.40 (m, 1 H), 3.54−3.72 (m, 1 H), 4.94 (d, *J* = 16 Hz, 1 H), 4.96 (d, *J* = 12 Hz, 1 H), 5.67 (ddd, *J* = 16, 12, 6.5 Hz, 1 H), 6.76−6.95 (m, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.16, 21.78, 26.36, 31.55, 34.44, 35.27, 43.48, 73.03, 77.86, 115.48 (q, $^1J_{CF}$ = 288 Hz), 117.87, 133.45, 157.21 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3150 cm^{-1}, 2966, 2878, 1702, 1530, 1202, 1182, 1140, 1074. − MS (70 eV, FD): *m/z* (%) = 268 (4), 252 (7), 196 (57), 97 (92), 83 (100), 69 (18), 55 (76), 41 (26).

(4R,1′S,2′R)-4-(1′,2′-Diphenyl-2′-trifluoroacetamido-1′-ethoxy)-4-methyl-1-hexene (**9a**): According to the general procedure 1, reaction of **2p** (381 mg, 1.00 mmol) for 4 d gave the homoallylic ether **9a** (398 mg, 0.98 mmol, 98%) as a colorless solid. M.p. 132°C; $[\alpha]_D^{20}$ = −42.7 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.0 Hz, 3 H), 1.03 (s, 3 H), 1.38 (q, *J* = 7.0 Hz, 2 H), 2.26−2.41 (m, 2 H), 4.96 (d, *J* = 3.5 Hz, 1 H), 5.05 (dd, *J* = 9.0, 3.5 Hz, 1 H), 5.15 (d, *J* = 12 Hz, 1 H), 5.16 (d, *J* = 16 Hz, 1 H), 5.88 (ddd, *J* = 16, 12, 9.0 Hz, 1 H), 6.88−7.02 (m, 4 H), 7.04−7.30 (m, 7 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.35, 23.02, 32.56, 43.45, 60.82, 76.35, 79.66, 116.85 (q, $^1J_{CF}$ = 289 Hz), 117.21, 126.08, 128.49, 129.52, 135.53, 139.41, 143.13, 156.23 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3324 cm^{-1}, 3070, 2980, 2934, 1702, 1562, 1208, 1180, 760, 700. − MS [70 eV, CI (NH_3)]: *m/z* (%) = 423 (100). − $C_{23}H_{26}F_3NO_2$ (405.5): calcd. C 68.13, H 6.46; found C 68.01, H 6.46.

General Procedure 2: Reaction of Aliphatic Ketones **1** *with Allylsilane* **3** *and the Chiral Reagent* **2p**: TfOH (18 µl, 0.20 mmol) was added at −78°C with stirring to a solution of ketones **1** (2.00 mmol), the chiral trimethylsilyl ether **2p** (381 mg, 1.00 mmol) and allyltrimethylsilane (**3**, 228 mg, 2 mmol) in CH_2Cl_2 (4 ml). Stirring was continued at −78°C. The reaction was quenched by addition of triethylamine (160 µl), the organic phase separated, the mixture poured into water (10 ml) and the aqueous phase extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel gave the appropriate homoallylic ethers **9a**−**e**.

(4R,1′S,2′R)-4-(1′,2′-Diphenyl-2′-trifluoroacetamido-1′-ethoxy)-4-methyl-1-heptene (**9b**): According to the general procedure 2, allylation of the ketone **1b** (173 mg, 2.00 mmol) with the diphenyl reagent **2p** (381 mg, 1 mmol) for 9 h gave the homoallylic ether **9b** (240 mg, 0.57 mmol, 57%) as colorless crystals. M.p. 144°C; $[\alpha]_D^{20}$ = +38.0 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.71 (t, *J* = 6.5 Hz, 3 H), 1.01 (s, 3 H), 1.11−1.45 (m, 4 H), 2.20−2.43 (m, 2 H), 4.95 (d, *J* = 4.0 Hz, 1 H), 5.05 (dd, *J* = 9.0, 4.0 Hz, 1 H), 5.14 (d, *J* = 14 Hz, 1 H), 5.15 (d, *J* = 17 Hz, 1 H), 5.86 (ddd, *J* = 17, 14, 7.5 Hz, 1 H), 6.86−7.05 (m, 4 H), 7.06−7.32 (m, 7 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.62, 17.35, 23.51, 42.34, 43.90, 59.57, 75.69, 79.55, 116.09 (q, $^1J_{CF}$ = 288 Hz), 118.32, 127.14, 127.80, 127.94, 128.09, 128.49, 134.34, 139.25, 140.15, 156.31 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3328 cm^{-1}, 3070, 3036, 2968, 2876, 1702, 1562, 1454, 1210, 1164, 1058, 700. − MS (70 eV, EI): *m/z* (%) = 378 (1), 292 (62), 203 (38), 179 (72), 111 (100), 69 (45), 55 (20), 41 (14). − $C_{24}H_{28}F_3NO_2$ (419.5): calcd. C 68.72, H 6.73; found C 68.66, H 6.76.

(4R,1′S,2′R)-4-(1′,2′-Diphenyl-2′-trifluoroacetamido-1′-ethoxy)-4-methyl-1-nonene (**9c**): According to the general procedure 2, allylation of the ketone **1c** (228 mg, 2.00 mmol) with the diphenyl reagent **2p** (381 mg, 1 mmol) for 4 d gave the homoallylic ether **9c** (236 mg, 0.53 mmol, 53%) as colorless crystals. M.p. 134°C; $[\alpha]_D^{20}$ = +29.5 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3 H), 1.02 (s, 3 H), 0.85−1.42 (m, 8 H), 2.21−2.43 (m, 2 H), 4.95 (d, *J* = 4.0 Hz, 1 H), 5.06 (dd, *J* = 9.0, 4.0 Hz, 1 H), 5.14 (d, *J* = 13 Hz, 1 H), 5.15 (d, *J* = 17 Hz, 1 H), 5.87 (ddd, *J* = 17, 13, 7.5 Hz, 1 H), 6.85−7.05 (m, 4 H), 7.06−7.30 (m, 7 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.92, 22.45, 23.30, 23.44, 32.10, 39.75, 43.65, 59.36, 75.48, 79.37, 115.89 (q, $^1J_{CF}$ = 288 Hz), 118.10, 126.97, 127.59, 127.72, 127.88, 128.30, 134.15, 136.06, 139.94, 156.11 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3348 cm^{-1}, 3070, 3036, 2938, 2862, 1704, 1556, 1456, 1208, 1178, 1062, 702. − MS (70 eV, EI): *m/z* (%) = 406 (1), 292 (100), 203 (43), 179 (56), 139 (61), 69 (8), 55 (10), 41 (4). − $C_{26}H_{32}F_3NO_2$ (447.5): calcd. C 69.78, H 7.21; found C 69.91, H 7.33.

(4S,1′S,2′R)-4,5-Dimethyl-4-(1′,2′-diphenyl-2′-trifluoroacetamido-1′-ethoxy)-1-hexene (**9d**): According to the general procedure 2, allylation of the ketone **1d** (173 mg, 2.00 mmol) with the diphenyl reagent **2p** (381 mg, 1 mmol) for 3 d gave the homoallylic ether **9d** (86 mg, 0.20 mmol, 20%) as colorless crystals. M.p. 150°C; $[\alpha]_D^{20}$ = +57.0 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (s, 3 H), 0.85 (d, *J* = 7.0 Hz, 3 H), 0.97 (d, *J* = 7.0 Hz, 3 H), 1.77 (sept, *J* = 7.0 Hz, 1 H), 2.40 (d, *J* = 7.5 Hz, 2 H), 4.98 (d, *J* = 4.0 Hz, 1 H), 5.09 (dd, *J* = 9.0, 4.0 Hz, 1 H), 5.16 (d, *J* = 10 Hz, 1 H), 5.18 (d, *J* = 17 Hz, 1 H), 5.85 (ddd, *J* = 17, 10, 7.5 Hz, 1 H), 6.85−7.04 (m, 4 H), 7.06−7.31 (m, 7 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.25, 17.29, 21.51, 35.32, 40.49, 59.50, 75.53, 81.23, 115.88 (q, $^1J_{CF}$ = 288 Hz), 118.21, 127.07, 127.66, 127.74, 127.92, 128.23, 133.85, 136.10, 139.90, 156.14 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3314 cm^{-1}, 3070, 3034, 2970, 2880, 1700, 1562, 1454, 1208, 1182, 1064, 700. − MS (70 eV, EI): *m/z* (%) = 378 (1), 292 (100), 203 (25), 179 (43), 111 (61), 69 (24), 55 (22), 41 (17). − $C_{24}H_{28}F_3NO_2$ (419.5): calcd. C 68.72, H 6.73; found C 68.69, H 6.76.

(4S,1′S,2′R)-4-Cyclohexyl-4-(1′,2′-diphenyl-2′-trifluoroacetamido-1′-ethoxy)-1-pentene (**9e**): According to the general procedure 2, allylation of the ketone **1e** (252 mg, 2.00 mmol) with the diphenyl reagent **2p** (381 mg, 1 mmol) for 3 d gave the homoallylic ether **9e** (65 mg, 0.14 mmol, 14%) as colorless crystals. M.p. 163°C; $[\alpha]_D^{20}$ = +28.7 (*c* = 1, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (s, 3 H), 0.88−1.44 (m, 5 H), 1.47−1.94 (m, 6 H), 2.38 (d, *J* = 7.0 Hz, 2 H), 4.95 (d, *J* = 3.5 Hz, 1 H), 5.07 (dd, *J* = 9.0, 3.5 Hz, 1 H), 5.17 (d, *J* = 10 Hz, 1 H), 5.19 (d, *J* = 17 Hz, 1 H), 5.85 (ddd, *J* = 17, 10, 7.0 Hz, 1 H), 6.82−7.05 (m, 4 H), 7.06−7.34 (m, 7 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.93, 26.58, 26.84, 27.15, 27.26, 40.54, 45.73, 59.48, 75.53, 81.13, 115.91 (q, $^1J_{CF}$ = 288 Hz), 118.19, 127.13, 127.66, 127.74, 127.91, 128.33, 133.99, 136.14, 139.95, 156.16 (q, $^2J_{CF}$ = 37 Hz). − IR (KBr): ν = 3348 cm^{-1}, 3070, 3036, 2958, 2938, 1702, 1554, 1456, 1208, 1178, 1100, 1062, 702. − MS (70 eV, EI): *m/z* (%) = 309 (2), 292 (93), 203 (55), 179 (63), 139 (100), 107 (46), 97 (23), 83 (44), 41 (19).

Synthesis of the Tertiary Homoallylic Alcohols **5** *from the Ethers* **9**: *(R)-4-Methyl-1-nonen-4-ol* (**5**, R = pentyl): A solution of the homoallylic ether **9c** (117 mg, 0.261 mmol) in THF (5 ml) was poured into liquid ammonia (100 ml) at −78°C with stirring and subsequently, sodium (30.0 mg, 1.31 mmol) was added. Stirring was continued for 15 min at −78°C and the reaction quenched by addition of solid NH_4Cl (500 mg). The ammonia was evaporated at room temp., then water (50 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel gave the

homoallylic alcohol **5** (R = pentyl, 36 mg, 0.23 mmol, 88%). $[\alpha]_D^{20} = -2.0$ (c = 1, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.5 Hz, 3 H), 1.01–1.75 (m, 8 H), 1.14 (s, 3 H), 2.21 (d, J = 7.5 Hz, 2 H), 5.10 (d, J = 18 Hz, 1 H), 5.13 (d, J = 10 Hz, 1 H), 5.85 (ddd, J = 18, 10, 7.5 Hz, 1 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.07, 22.67, 23.52, 26.70, 32.37, 46.25, 72.17, 118.53, 134.08. – IR (film): ν = 3394 cm^{-1}, 2958, 2932, 2872, 1464, 1156. – MS (70 eV, EI): *m/z* (%) = 141 (2), 115 (93), 87 (100), 71 (13), 55 (48), 45 (59), 43 (44), 41 (30).

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